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GHGT-9

## Mass transfer in a small scale post-combustion flue gas absorber, experiment and modelling

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### Abstract<sup>\*</sup>

Carbon dioxide can be removed from flue gas streams with aqueous solutions of alkanolamines. In the absorber carbon dioxide is contacted with the solvent and due to several chemical reactions the carbon dioxide is converted into ionic species. These species are non-volatile and remain in the liquid phase until the carbon dioxide is released in the stripper (by adding heat). For the design of gas treating processes a sound fundamental process model is required in which all relevant mass transfer aspects, thermodynamics and kinetics are incorporated. However, the quality of a process model should always be determined by the validation with experimental data. In this study a rate-based model of a flue gas absorber is compared quantitatively with experimental data derived from a continuous absorber – stripper pilot plant which was operated at typical post-combustion flue gas conditions.

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**Keywords:** absorption; mass transfer; alkanolamine; post-combustion CO<sub>2</sub> capture; rate-based

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### 1. Introduction

In this study experiments in a CO<sub>2</sub> capture pilot plant, designed for post-combustion CO<sub>2</sub>-capture, have been carried out and the results of these experiments have been compared to the outcome of the simulations of a rate-based absorption model. In this process model the mass transfer, thermodynamics and kinetics are included. In this study the performance of the solvent in the absorber is studied in detail.

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## 2. Experimental set-up

The experimental set-up used in this work has been designed, built and operated by Shell Global Solutions as part of the Dutch CAPTECH program. The unit has been designed to test the performance of different solvents for the capture of CO<sub>2</sub> from gas streams. The unit consists of an absorber and a desorber. A schematic representation of the pilot plant is presented in Figure 1.

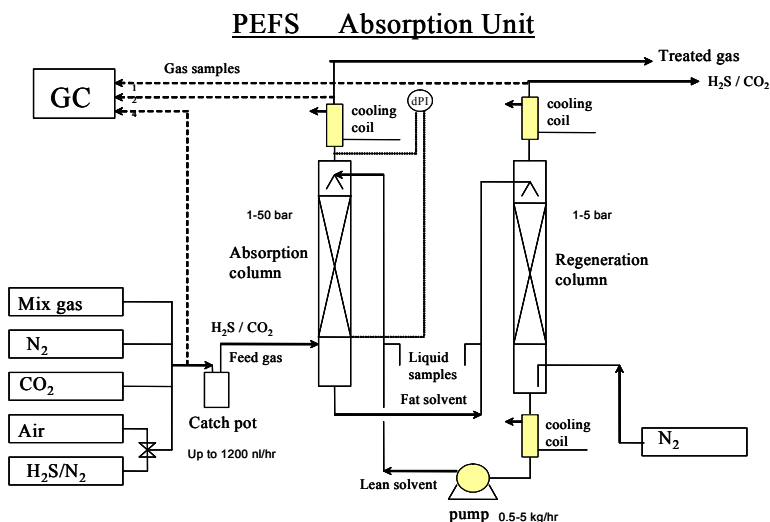


Figure 1 Simplified flow scheme of the CAPTECH pilot plant unit at Shell Global Solutions.

The unit can handle a total gas flow up to 1.3 Nm<sup>3</sup>/h and a liquid circulation flow of 6 kg/h. In this study the performance of the absorber of this pilot plant has been studied. The absorber has a diameter of 2.5 cm and a height of 1.45 meter. The absorber is filled with structured packing, i.e. Sulzer EX laboratory packing with a geometrical interfacial area of 1735 m<sup>2</sup>/m<sup>3</sup>.

The CO<sub>2</sub> is premixed with nitrogen and fed to the bottom of the absorber, where it is counter-currently contacted with the solvent. The CO<sub>2</sub> is transferred from gas to liquid phase and will react with the solvent to several non-volatile (ionic) species. The treated gas is leaving the top of the absorber. The CO<sub>2</sub> concentration of the vapour in- and outlet stream is analysed by means of a gas chromatograph. The (CO<sub>2</sub>) rich solvent is sent to the regenerator in which part of the CO<sub>2</sub> is released from the solvent. The (CO<sub>2</sub>) lean solvent is routed back to the top of the absorber. In this study the performance of aqueous 50 wt.% MDEA solutions is studied in the post combustion CO<sub>2</sub> capture pilot plant.

## 3. Rate-based model

In this study a rate-based simulation model is used, to describe the absorber of the pilot plant. For details about this rate-based model reference is made to van Loo et al. [1]. In this model, an absorber can be simulated with a tray to tray (or segment to segment) procedure for several blends of aqueous amine solvents. The mass transfer model with complex, reversible, multiple chemical reactions included, describes the absorption of CO<sub>2</sub> in an aqueous solution of an amine blend. For a more detailed overview the reader is referred to Versteeg et al. [2, 3]. The absorption rate of CO<sub>2</sub> is calculated in combination with the concentration profiles near the gas-liquid interface for all reactants and products. In the model kinetic data of the several chemical reactions are incorporated and the thermodynamic model used is based on ideal activities (one). A kind of Kent-Eisenberg [8] approach has been used to correct for the non-idealities in the liquid phase.

The following amines are included in the database of the rate-based model:

- MDEA, DMMEA, DEMEA, TEA (tertiary amines)
- MEA, DEA, MMEA, DIPA, DGA, AMP (primary and secondary amines)

The following input data are required to simulate the absorber:

- Solvent type and composition;
- Gas and liquid inlet temperatures;
- In- and outlet CO<sub>2</sub> concentrations of the gas stream;
- CO<sub>2</sub> concentration of the inlet solvent;
- Mass transfer parameters:  $k_G$ ,  $k_L$  and  $a$ ;
- Physical properties (density and heat capacity);
- Reaction and absorption enthalpy;

The following data are calculated by the model:

- Required absorber dimensions;
- Temperature profile in the absorber;
- Concentration profile in the absorber;
- Profile of the speciation in the liquid phase.

## 4. Results

### 4.1. Sensitivity study

Initially the sensitivity of the mass transfer parameters has been evaluated. The influence of the mass transfer parameters  $k_L$  (Figure 2),  $k_G$  (Figure 3) and  $a$  (Figure 4) has been verified. In these figures the CO<sub>2</sub> outlet gas concentration is plotted as function of column length; the bottom of the column corresponds with an absorber length of zero. In the figures below the absorber length is calculated for a gas stream with a 6.5 kPa CO<sub>2</sub> inlet partial pressure and a 2.0 kPa CO<sub>2</sub> outlet partial pressure.

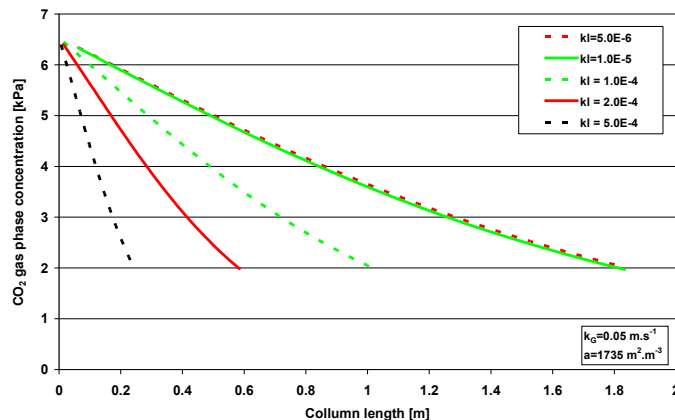


Figure 2 Influence of liquid side mass transfer coefficient ( $k_L$  in  $\text{m.s}^{-1}$ ) on the absorber dimensions

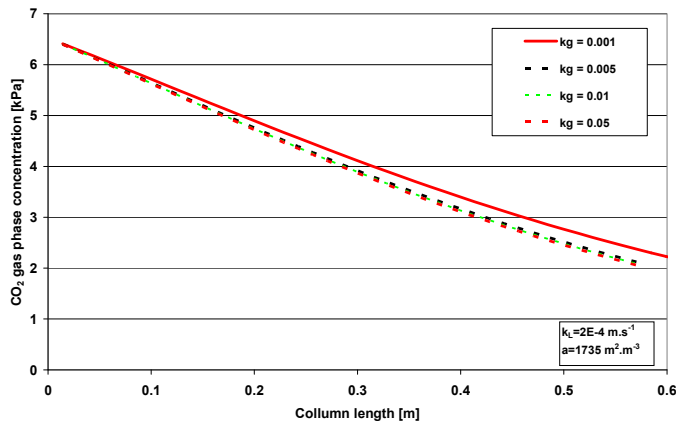


Figure 3 Influence of the gas side mass transfer coefficient ( $k_G$  in  $\text{m.s}^{-1}$ ) on the absorber dimensions

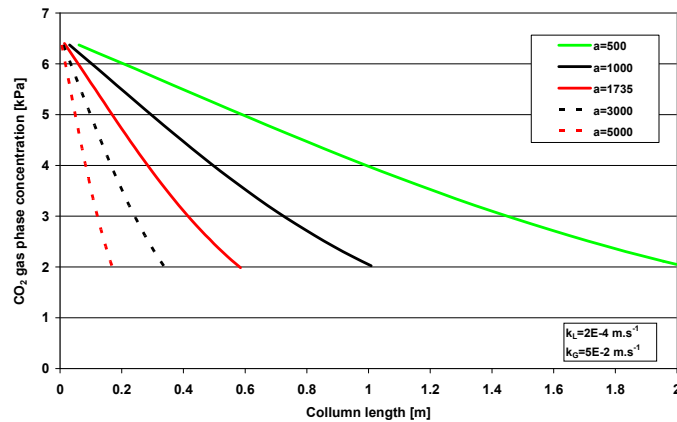


Figure 4 Influence of the interfacial area ( $a$  in  $\text{m}^2.\text{m}^{-3}$ ) on the absorber dimensions

From these figures the following conclusions can be derived:

- An increasing liquid side mass transfer coefficient ( $k_L$ ) will result in a decreasing absorber size. However, when the value of this parameter is less than  $1\text{E-}5 \text{ m.s}^{-1}$ , the absorber size is no longer affected. This can be explained by the fact that at low  $k_L$  values, the reaction regime ( $\text{CO}_2$ -solvent) is changing from not enhanced to pseudo first order. In this pseudo first order regime, the reaction is enhancing the mass transfer of  $\text{CO}_2$  to the liquid phase. The chemical enhancement is calculated and equals the Hatta number ( $Ha$ ). From the equations below it can be concluded that the absorption rate and thus the absorber dimensions become independent of the liquid side mass transfer parameter ( $k_L$ ) in case the reaction is taking place in the pseudo first order regime:

$$J = k_L E (mC_G - C_L) \quad (1)$$

$$E = Ha = \frac{\sqrt{k_{1,1} C_{am} D_{CO_2}}}{k_L} \quad (2)$$

$$J = \sqrt{k_{1,1} C_{am} D_{CO_2}} (m C_G - C_L) \quad (3)$$

- From Figure 3, where typical values around  $0.01 \text{ m.s}^{-1}$  for the gas side mass transfer coefficient ( $k_G$ ) have been used, it can be concluded that the value of this parameter hardly affects the required absorber dimensions;
- From Figure 4 it can be seen that the required absorber length is significantly affected by the interfacial area ( $a$ ). The higher this interfacial area, the smaller the required absorber length.

For the pilot plant simulations, the mass transfer parameters as described above have been calculated from the several correlation which are available in the literature.

During the experiments with aqueous MDEA the lean loading entering the top of the absorber was not determined experimentally. Therefore the influence of this parameter on the calculated absorber size has been calculated. In Figure 5 the influence of the lean liquid loading on the required absorber length can be seen.

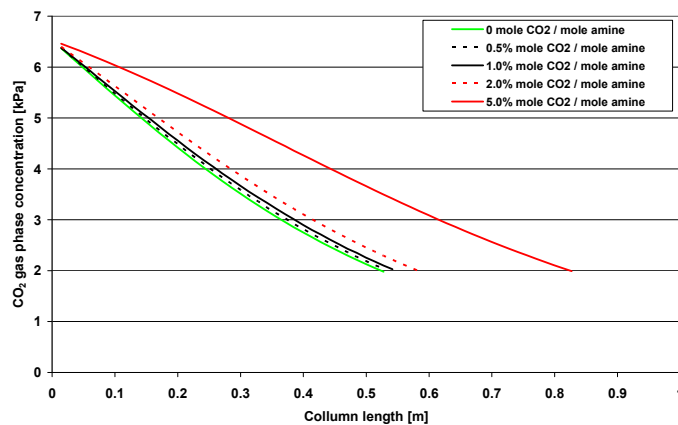


Figure 5 Influence of the  $\text{CO}_2$  loading of the lean aqueous MDEA solvent on the absorber performance

From Figure 5 it can be concluded that there is hardly any influence of the  $\text{CO}_2$  lean liquid loading, provided that the loading is less than 0.02 mole  $\text{CO}_2$  per mole amine. However, if this lean liquid loading is increasing from 0.02 to 0.05 mole  $\text{CO}_2$  per mole amine the required absorber length increases from 0.6 to 0.8 meter. In this study it is assumed that the lean loading of the solvent entering the absorber is 0.02 mole  $\text{CO}_2$  / mole amine (or less).

#### 4.2. Pilot plant simulations

A vast amount of experiments have been carried out with aqueous MDEA in the pilot plant. In this study one experiment was selected and analysed in detail. The experiment with the lowest error (2.3 %) in  $\text{CO}_2$  mass balance was further studied.

Before the length of the absorber can be calculated from the input parameters as stated in chapter 3, the mass transfer parameters ( $k_L$ ,  $k_G$  and  $a$ ) need to be known. These parameters have been estimated from empirical correlations as available in literature. Several correlations to estimate these mass transfer parameters have been evaluated and an average of these parameters was used as input for the absorber simulations with the rate-based model.

The following values were used:

- Liquid side mass transfer coefficient  $k_L = 2.9 \text{ E-5 m.s}^{-1}$ ; this value is based on an average of the  $k_L$  calculated according the method of Bravo, Rocha and Fair 1985 [1] and Bravo, Rocha and Fair 1992 [5];
- Gas side mass transfer coefficient  $k_G = 4.0 \text{ E-3 m.s}^{-1}$ ; this value is based on an average of the  $k_L$  calculated according the method of Bravo, Rocha and Fair 1985 [1] and Bravo, Rocha and Fair 1992 [5];
- Interfacial area  $a = 1500 \text{ m}^2.\text{m}^{-3}$ ; this value is based on an average of the area calculated according the method of Bravo, Rocha and Fair 1985 [1], Onda, Takeuchi and Okumoto 1968 [6] and Delft model Olujic [7].

When these mass transfer parameters were calculated the absorber performance can be simulated. In Figure 6 the calculated gas phase concentration as function of column length is presented.

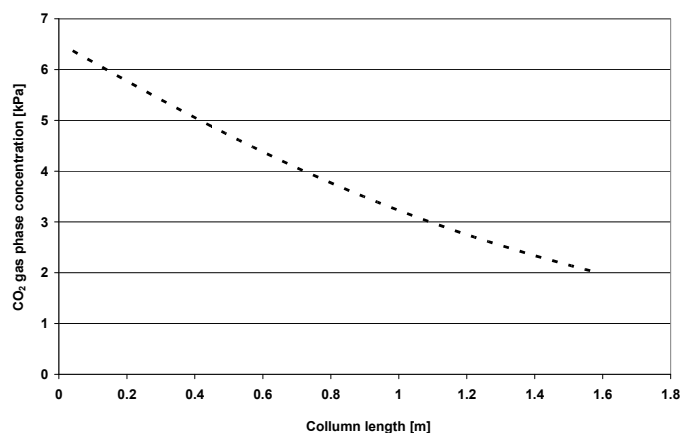


Figure 6 Calculated CO<sub>2</sub> gas phase concentration as function of column length (length=0 is absorber bottom)

From this figure it can be concluded that according the absorption simulation model, the CO<sub>2</sub> concentration of the gas entering the top (6.5 kPa) is removed to the gas outlet concentration (2 kPa) in an absorber with a packed height of 1.6 m. So the model calculation is in good agreement with the experiment as carried out in the pilot plant, because the pilot plant consists of an absorber with a packed height of 1.45 m.

In Figure 7 the CO<sub>2</sub> flux and chemical enhancement, as calculated by the model, is presented as function of CO<sub>2</sub> partial pressure.

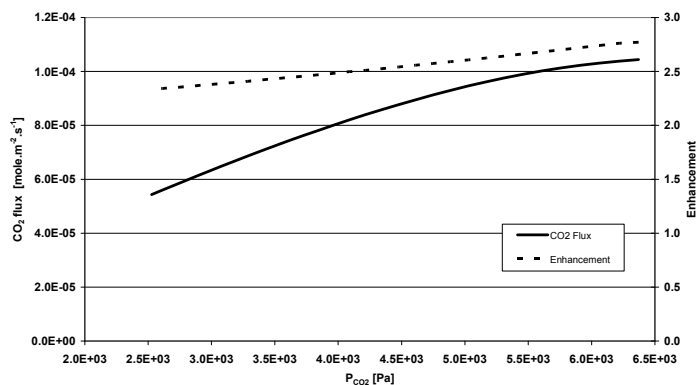


Figure 7 Absorption flux and chemical enhancement of CO<sub>2</sub> in 50 wt.% aqueous MDEA as calculated by the rate-based model

In the bottom of the absorber (high  $\text{CO}_2$  partial pressure) the highest flux is observed, i.e.  $1.0\text{E-}4 \text{ mole.m}^{-2}.\text{s}^{-1}$ . In the top the  $\text{CO}_2$  flux is decreasing to 50 % of this value ( $5.4 \text{E-}5 \text{ mole.m}^{-2}.\text{s}^{-1}$ ). The chemical enhancement is the value by which the flux is enhanced due to the reaction compared to a system without a chemical reaction. In the simulated absorber the chemical enhancement (E) is decreasing from 2.8 (bottom) to 2.3 (top). So it can be concluded that the mass transfer of  $\text{CO}_2$  to the liquid phase is only slightly enhanced by a chemical reaction in the absorber.

For the mass transfer calculations not only the total  $\text{CO}_2$  solubility is important, also the speciation (concentration of all species) in the liquid phase is important. In Figure 8 the calculated liquid speciation is presented as function of  $\text{CO}_2$  liquid loading.

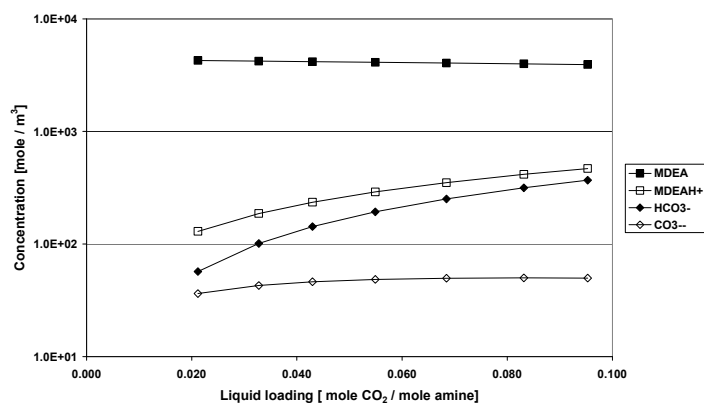


Figure 8 Speciation of the liquid phase as function of  $\text{CO}_2$  liquid loading

In Figure 8 it can be seen that the  $\text{CO}_2$  present in the liquid phase is mostly present as bicarbonate. The concentration carbonate is approximately an order of magnitude lower than the bicarbonate concentration. The concentration molecular  $\text{CO}_2$  present in the liquid phase is not presented in Figure 8, because this concentration was very low, i.e. between 0.02 and 0.6  $\text{mole.m}^{-3}$ . In Figure 8 the bicarbonate, carbonate and protonated MDEA is increasing with increasing  $\text{CO}_2$  liquid loading. The minimum  $\text{CO}_2$  liquid loading (0.02) corresponds with the conditions in the top of the absorber, while the maximum  $\text{CO}_2$  liquid loading is reached in the bottom of the absorber.

## 5. Conclusion

In this study pilot plant data of a  $\text{CO}_2$  capture plant have been compared with a rate-based model. With the pilot plant experimental data were derived at typical post-combustion  $\text{CO}_2$  capture conditions. The  $\text{CO}_2$  capture experiments were carried out with an aqueous 50 wt.% MDEA solvent. With the rate-based model an absorber can be calculated with a segment-to-segment procedure for several blends of aqueous amine solvents. Mass transfer, reaction kinetics and thermodynamics are included in the simulation model. With this model it was possible to predict the size of an absorber within an accuracy of 10 %. Also the  $\text{CO}_2$  flux, chemical enhancement and liquid speciation were calculated with the model.



## 6. Future work

The rate-based model used in this work is the precursor of a more advanced activity and rate-based simulator that is currently under development [9] and is expected to describe the system in much more detail and with much larger accuracy and no longer requires any adjustments to match the VLE data. Also this new simulator no longer requires user-defined mass transfer parameters, density, heat capacity and heat of reaction data since these values are directly derived from thermodynamic or literature correlations.

## 7. Acknowledgement

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Shell Global Solutions is greatly acknowledgement for their contribution to the experimental part of this work.

## 8. Symbol List

A	interfacial area	$[\text{m}^2.\text{m}^{-3}]$
$C_{\text{am}}$	amine concentration	$[\text{mol}.\text{m}^{-3}]$
$C_G$	concentration is gas phase	$[\text{mol}.\text{m}^{-3}]$
$C_L$	concentration is liquid phase	$[\text{mol}.\text{m}^{-3}]$
$D_{\text{CO}_2}$	diffusion coefficient of $\text{CO}_2$ in liquid phase	$[\text{m}.\text{s}^{-2}]$
E	chemical enhancement	$[-]$
Ha	Hatta number	$[-]$
J	flux	$[\text{mol}.\text{m}^{-2}.\text{s}^{-1}]$
$k_{1,1}$	kinetic rate constant	$[\text{m}^3.\text{mol}^{-1}.\text{s}^{-1}]$
$k_G$	gas side mass transfer coefficient	$[\text{m}.\text{s}^{-1}]$
$k_L$	liquid side mass transfer coefficient	$[\text{m}.\text{s}^{-1}]$
m	physical solubility ( $=C_L/C_G$ at equilibrium)	$[-]$
MDEA	N-methyldiethanolamine	$[-]$

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